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# Dioxolanylium Ions Derived from Carbohydrates. III. Reaction of Arabinopyranoside Derivatives with Nucleophiles

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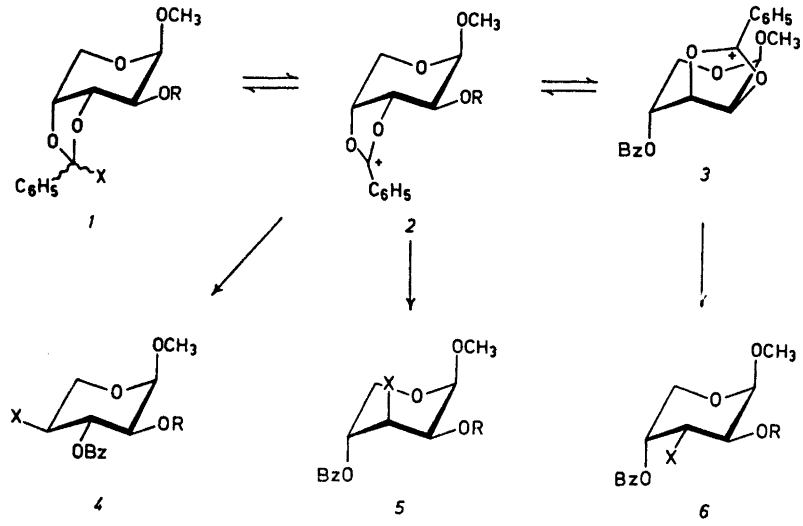
Treatment of methyl 2-*O*-benzoyl- (or 2-*O*-*p*-toluenesulfonyl-) 3,4-*O*-benzylidene-β-D-arabinopyranoside with triphenylmethyl fluoroborate gave 3,4-benzoxonium ions (*2a* or *2b*). The reaction of these benzoxonium ions with a number of nucleophiles has been studied. With chloride, bromide, iodide, thiocyanate, tosylate, and trifluoroacetate *trans* opening of the benzoxonium ion took place. With fluoride, acetate, azide, amides, cyanide, and methoxide orthoacid derivatives were formed; these on subsequent reaction with water underwent *cis* opening to give hydroxy benzoates.

In the preceding papers of this series [1,2] it was shown that benzylidene derivatives of carbohydrates in certain cases can be converted into benzoxonium ions by using triphenylmethyl fluoroborate as a hydride abstractor. The resulting benzoxonium ions reacted with water to give *cis* hydroxy benzoates; with bromide ion *trans* bromo deoxybenzoates were obtained. A *trans* opening of dioxolanylium ions with nucleophiles may provide a method for introduction of functional groups into carbohydrates. The reaction of benzoxonium ions with a variety of nucleophiles has therefore been investigated with pentopyranose derivatives as substrates.

An equilibrium mixture of the two benzoxonium ions *2a* and *3* in acetonitrile solution was prepared as described previously.[1] Treatment of this mixture with chloride or iodide ion gave a mixture of the 4-halo-L-xylose and 3-halo-D-arabinose derivatives (*4a* and *6a*, respectively). The ratio *4a*:*6a* was 6:1 in case of the chlorides and 1:2 with the iodides while bromide ion (previously reported [1]) gave the two products in approximately equal amounts, signifying a difference in reactivity of the two ions *2a* and *3* towards the different halide ions.

Treatment of the ions *2a* and *3* with fluoride ion did not give any fluoro deoxybenzoate. After hydrolysis of the reaction mixture the hydroxy benzoate *6a* (X = OH) was obtained. This could mean that the ion *2a*, (or *3*) did not react with fluoride. However, a $^1$H NMR spectrum of the solution, measured shortly after addition of sodium fluoride, showed that the characteristic low field signals of the benzoxonium ion [1] had disappeared. The $^1$H NMR spectrum gave no further information, but a $^{19}$F NMR spectrum showed a signal at 53 ppm upfield from fluoroform which indicated that an orthoacid fluoride (*1a*, X = F) was formed.[3] This compound was stable for at least 24 h at room temperature, but decomposed when heated overnight at 70 °C. The hydroxy benzoate *6a* (X = OH) was probably formed by hydrolysis of *1a* (X = F).

Reaction of the ions *2a* and *3* with *p*-toluenesulfonate ion resulted in *trans* opening of the benzoxonium ion and formation of the L-xylose derivative *4a* (X = OTs) and the D-arabinose derivative *6a* (X = OTs) in approximately equal amounts. Treatment of the mixture of *2a* and *3* with cyanide or with methanol gave, on the other hand, only the orthoacid derivatives *1a* (X = CN) and *1a* ($X = OCH_3$), respectively. Two epimers may arise in each case; but in both cases one epimer was strongly favoured, probably the *endo* phenyl compound.[4] The orthoacid ester *1a* ($X = OCH_3$) was completely converted into *6a* (X = OH) on treatment with methanol and aqueous acid.



a: R = Bz
b: R = Ts

In order to simplify the reaction mixtures a number of experiments were carried out with methyl 3,4-*O*-benzylidene-2-*O*-*p*-toluenesulfonyl-β-D-arabinopyranoside (*1b*, X=H). On treatment with triphenylmethyl fluoroborate it gave the benzoxonium ion *2b*, which was characterized through its $^{1}H$ and $^{13}C$ NMR spectra. Since no neighbouring group effect is expected from the 2-*O*-*p*-toluenesulfonyl group only one benzoxonium ion is present in this case.

Reaction of *2b* with water gave exclusively the axial 4-*O*-benzoate *6b* (X=OH).[5] With bromide ion *2b* predominantly gave the 4-bromo-L-xylose derivative *4b* (X=Br) and only a small amount of the 3-bromo-D-lyxose derivative *5b* (X=Br), indicating a preference of *ca.* 10:1 for attack at C4 relative to C3. Treatment of the ion *2b* with thiocyanate ion for 5 h followed by hydrolysis gave the hydroxy benzoate *6b* (X=OH) only. When *2b* was allowed to react with thiocyanate for 5 days *trans* opening took place and the 4-thiocyanato-L-xylose and 3-thiocyanato-D-lyxose derivatives, *4b* and *5b* (X=−SCN), respectively, were isolated. The distinction between thiocyanate and isothiocyanate structures was based on IR spectroscopy.[6] Reaction of *2b* with trifluoroacetate ion also resulted in *trans* opening of the benzoxonium ion to give *4b* ($X=CF_3COO-$) which was directly hydrolysed to the *trans*-hydroxy benzoate *4b* (X=OH). The latter sequence provides an indirect method for *trans* opening of dioxolanylium ions with water.

In attempts to introduce a nitrogen function into the pyranose ring, the benzoxonium ion *2b* was treated with azide and phthalimide ion and with acetamide. In no case, however, did *trans* opening of the ion take place. Addition of azide ion to the acetonitrile solution of *2b* caused all $^{1}H$ NMR signals of the latter to disappear at once. The resulting product was stable for at least 5 days at room temperature and was converted to the hydroxy benzoate *6b* (X=OH) upon addition of water. The NMR spectrum of the primary product, formed from *2b* and azide ion was not well resolved, and there is therefore no direct evidence for an orthoacid type of compound (*1b*, $X=N_3$). However, the formation of *6b* (X=OH) on hydrolysis indicates that such a compound was indeed formed.

Treatment of *2b* with acetamide gave two unstable *N*-acetylated orthoamides (*1b*, $X=CH_3CONH-$) which were isolated and characterized by $^{1}H$ NMR spectroscopy. On hydrolysis they yielded *6b* (X=OH).

Reaction of *2b* with sodium fluoride gave an unstable orthoacid fluoride (*1b*, X = F). This was not hydrolysed, but instead treated with trimethyl phosphite to give two epimeric phosphonium derivatives [*1b*, X = $-P^+(OCH_3)_3$], isolated as the phosphonates *1b* [X = $-P(O)(OCH_3)_2$] after further treatment with bromide ion. $^{13}C$ NMR spectra of the latter products exhibited the large one-bond $^{31}P-^{13}C$ coupling in the low field signal of the "benzylic" carbon. The same two phosphonates were obtained by direct treatment of *2b* with trimethyl phosphite followed by reaction with bromide.

It is generally found that reaction of dioxolanylium ions with acetate ion leads to *trans* opening.[7] Such reactions have usually been carried out with anhydrous acetic acid as the solvent.[8,9] However, treatment of the benzoxonium ion *2b* with sodium acetate in acetonitrile solution did not result in *trans* opening, even after 5 days at room temperature. When the reaction was studied by $^{13}C$ NMR spectroscopy it was found that the low field signals of C3 and C4 (84 and 87 ppm, respectively) of the ion *2b* shifted to *ca.* 74 ppm immediately after acetate ion was added. This indicates that an orthoacid derivative (*1b*, X = OAc) is formed and in agreement herewith the hydroxy benzoate *6b* (X = OH) was obtained on hydrolysis. The reaction of other benzoxonium ions with acetate will be discussed in the following paper.

## EXPERIMENTAL

Thin layer chromatography (TLC) was performed on Silica gel $PF_{254}$ (Merck); for preparative work 1 mm layers were used on 20 × 40 cm plates. Compounds were visualised by UV light. Melting points are uncorrected. Optical rotations were measured in chloroform solution on a Perkin Elmer 141 instrument. $^1H$ NMR spectra were measured on Bruker HXE-90 and HX-270 instruments, $^{19}F$ and $^{31}P$ spectra on HXE-90, and $^{13}C$ NMR spectra on a Bruker WH-90 instrument as previously recorded. All spectra were measured in deuteriochloroform solutions unless otherwise specified. Chemical shifts of $^{31}P$ spectra are relative to phosphoric acid.

*Methyl 3,4-O-benzylidene-2-O-p-toluenesulfonyl-β-D-arabinopyranoside* (1b). Crude methyl 3,4-*O*-benzylidene-β-D-arabinopyranoside (from 4.92 g of methyl β-D-arabinopyranoside)[1] was treated overnight with *p*-toluenesulfonyl chloride (7.5 g) in pyridine (25 ml). Precipitation of the tosylate with water and recrystallization from ethanol gave 6.7 g (55 %) of *1b* as a mixture of diastereomers,[10] m.p. 103 – 122 °C.

*Treatment of benzoxonium ions with nucleophiles. General procedure.* The benzoxonium ions (*2* and *3*) were prepared by treatment of the benzylidene compound with triphenylmethyl fluoroborate in acetonitrile solution as described previously.[1] To this solution was added 3 – 5 molar equivalents of the appropriate nucleophile (dried over phosphorus pentoxide or conc. sulfuric acid) and the mixture was stirred at room temperature for the time specified under the individual nucleophiles. The reaction mixture was then stirred for 5 min with 10 ml of saturated, aqueous $NaHCO_3$ and extracted with chloroform. The chloroform solution was washed with water, dried and concentrated. Preparative TLC using ether-pentane (1:1) as the eluent (unless otherwise specified) gave triphenylmethane, moving with the solvent front, followed by triphenylcarbinol and the products.

*Ions* 2a *and* 3 *from methyl 2-O-benzoyl-3,4-O-benzylidene-β-D-arabinopyranoside* (1a, X = H). *Fluoride ion.* The benzylidene compound (*1a*, X = H) (747 mg) was converted to the benzoxonium ion and stirred with 209 mg of sodium fluoride for 2 h. Work-up as described above gave 517 mg (66 %) of methyl 2,4-di-*O*-benzoyl-β-D-arabinopyranoside (*6a*, X = OH), m.p. 140 – 142 °C, identical with the product described previously.[1]

*Chloride ion.* The benzoxonium ion from (*1a*, X = H) (593 mg) was stirred for 6 h with tetraethylammonium chloride (1.0 g). Work-up and chromatography gave three products. The fastest-moving fraction gave 412 mg (63 %) of methyl 2,3-di-*O*-benzoyl-4-chloro-4-deoxy-α-L-xylopyranoside (*4a*, X = Cl), m.p. 120 – 121 °C after recrystallization from cyclohexane, $[\alpha]_D^{20}$ −142° (*c* 1.6). Anal. $C_{20}H_{19}ClO_6$: C, H, Cl. $^1H$ NMR: δ 5.15 (H1), 5.12 (H2), 5.95 (H3), 4.16 (H4), 3.93 (H5 and H5′); $J_{12}$ = 3.5 Hz, $J_{23}$ = 10.0, $J_{34}$ = 9.5, $J_{45}$ = 7.5, $J_{45'}$ = 9.5.

The second fraction (71 mg, 11 %) consisted of methyl 2,4-di-*O*-benzoyl-3-chloro-3-deoxy-β-D-arabinopyranoside (*6a*, X = Cl) as a syrup, $[\alpha]_D^{20}$ −237° (*c* 2.2). Anal. $C_{20}H_{19}ClO_6$: C, H, Cl. $^1H$ NMR: δ 5.17 (H1), 5.57 (H2), 4.76 (H3), 5.57 (H4), 4.06 (H5), 3.98 (H5′); $J_{12}$ = 3.4 Hz, $J_{23}$ = 11.1, $J_{34}$ = 3.3, $J_{45}$ = 1.6, $J_{45'}$ = 1.9, $J_{55'}$ = 13.1.

A third fraction (43 mg) was impure methyl 2,4-di-*O*-benzoyl-3-chloro-3-deoxy-β-D-lyxopyranoside (*5a*, X = Cl), only characterized through its $^1H$ NMR spectrum: δ 4.88 (H1), 5.72 (H2), 4.51 (H3), 5.47 (H4), 4.51 (H5), 3.67 (H5′); $J_{12}$ = 2.7 Hz, $J_{23}$ = 4.0, $J_{34}$ = 6.3, $J_{45}$ = 3.3, $J_{45'}$ = 5.6, $J_{55'}$ = 12.5.

A small amount (32 mg, 4 %) of *6a*, X = OH was also isolated.

*Iodide ion.* The benzoxonium ion from *1a*, X = H (424 mg) was stirred with potassium

iodide for 5 h. Work-up and chromatography gave three products.

The fast-moving fraction (143 mg, 25 %) gave methyl 2,3-di-*O*-benzoyl-4-iodo-4-deoxy-α-L-xylopyranoside (*4a*, X = I), m.p. 140 – 141 °C after recrystallization from ethyl acetate-pentane, $[\alpha]_D^{21}$ −105° (*c* 1.0). Anal. $C_{20}H_{19}IO_6$: C, H, I. $^1$H NMR: δ 5.22 (H1), 5.11 (H2), 6.01 (H3), 4.23 (H4), 4.13 (H5), 3.94 (H5′); $J_{12}$ = 3.4 Hz, $J_{23}$ = 9.7, $J_{34}$ = 10.1, $J_{45}$ = 12.0, $J_{45'}$ = 4.4, $J_{55'}$ = 10.5.

The second fraction (224 mg, 39 %) gave methyl 2,4-di-*O*-benzoyl-3-iodo-3-deoxy-β-D-arabinopyranoside (*6a*, X = I) as a syrup, $[\alpha]_D^{25}$ −289° (*c* 2.3). Anal. $C_{20}H_{19}IO_6$: C, H, I. $^1$H NMR: δ 5.10 (H1), 5.59 (H2), 4.94 (H3), 5.52 (H4), 4.09 (H5), 3.90 (H5′); $J_{12}$ = 3.3 Hz, $J_{23}$ = 11.7, $J_{34}$ = 3.2, $J_{45}$ = 1.3, $J_{45'}$ = 1.7, $J_{55'}$ = 12.9.

The third fraction (26 mg, 5 %) was methyl 2,4-di-*O*-benzoyl-3-deoxy-3-iodo-β-D-lyxopyranoside (*5a*, X = I), m.p. 134 – 136 °C after recrystallization from ethyl acetate-pentane. Anal. $C_{20}H_{19}IO_6$: C, H. $^1$H NMR: δ 4.92 (H1), 5.41 (H2), 4.64 (H3), 5.58 (H4), 4.57 (H5), 3.68 (H5′); $J_{12}$ = 2.5 Hz, $J_{23}$ = 4.0, $J_{34}$ = 6.1, $J_{45}$ = 3.4, $J_{45'}$ = 6.1, $J_{55'}$ = 12.5.

In addition 41 mg (9 %) of *6a*, X = OH was isolated.

p-*Toluenesulfonate ion*. Benzoxonium ion from 628 mg of *1a* (X = H) was stirred overnight with 1.1 g of tetraethylammonium *p*-toluenesulfonate. Work-up and chromatography gave 473 mg (51 %) of a mixture (45:55) of two products. Crystallization from chloroform (5 ml)-pentane (10 ml) yielded 191 mg (21 %) of methyl 2,3-di-*O*-benzoyl-4-*O*-*p*-toluenesulfonyl-α-L-xylopyranoside (*4a*, X = TsO), m.p. 172 – 173 °C, $[\alpha]_D^{21}$ −112° (*c* 1.8). Anal. $C_{27}H_{26}O_9S$: C, H, S. $^1$H NMR: δ 5.10 (H1), 5.24 (H2), 6.04 (H3), 4.91 (H4), 4.05 (H5), 3.86 (H5′); $J_{12}$ = 3.5 Hz, $J_{23}$ = 9.9, $J_{34}$ = 9.3, $J_{45}$ = 6.4, $J_{45'}$ = 10.6, $J_{55'}$ = 11.0.

Preparative TLC of the mother liquor (ether-pentane 3:1) gave 55 mg of a mixture and 177 mg (19 %) of methyl 2,4-di-*O*-benzoyl-3-*O*-*p*-toluenesulfonyl-β-D-arabinopyranoside (*6a*, X = TsO), m.p. 127 – 130 °C. The product was identical with a sample prepared by tosylation of methyl 2,4-di-*O*-benzoyl-β-D-arabinopyranoside [1] with *p*-toluenesulfonyl chloride in pyridine, m.p. 131 – 132 °C, $[\alpha]_D^{21}$ −220° (*c* 1.0). Anal. $C_{27}H_{26}O_9S$: C, H, S. $^1$H NMR in a 1:1 mixture of benzene-$d_6$ and acetone-$d_6$: δ 5.16 (H1), 5.57 (H2), 5.35 (H3), 5.50 (H4), 4.00 (H5), 3.90 (H5′); $J_{12}$ = 3.3 Hz, $J_{23}$ = 10.2, $J_{34}$ = 3.4, $J_{45}$ = 1.4, $J_{45'}$ = 2.0, $J_{55'}$ = 13.3.

*Cyanide ion*. Benzoxonium ion from 536 mg of *1a* (X = H) was stirred overnight with 1.0 g of finely powdered potassium cyanide. Chromatography yielded 317 mg (55 %) of methyl 2-*O*-benzoyl-3,4-*O*-cyanobenzylidene-β-D-arabinopyranoside (*1a*, X = CN). Crystallization from ether and recrystallization from ethyl acetate-pentane gave a product with m.p. 130 – 131 °C, $[\alpha]_D^{23}$ −194° (*c* 1.1). Anal. $C_{21}H_{19}NO_6$: C, H. N. IR: 2235 cm$^{-1}$ (CN). $^1$H NMR in benzene-$d_6$: δ 4.87 (H1), 5.36 (H2), 4.68 (H3), 4.29 (H4), 3.83 (H5), 3.48 (H5′); $J_{12}$ = 3.4 Hz, $J_{23}$ = 7.8, $J_{34}$ = 6.3, $J_{45}$ < 0.5, $J_{45'}$ = 3.0, $J_{55'}$ = 13.9.

*Methanol*. Benzoxonium ion from 520 mg of *1a* (X = H) was poured into 0.5 ml of methanol in pyridine (5 ml) and stirred for 5 min. The mixture was diluted with methylene chloride (25 ml) and worked up as described above. Chromatography gave two products. Both the fast-moving (45 mg, 8 %) and the slow-moving fraction (324 mg, 58 %) gave $^1$H NMR spectra which corresponded to an orthoester. $^1$H NMR (fast moving fraction): δ 5.04 (H1), 5.65 (H2), 4.67 (H3), 4.23 (H4), 4.11 (H5), 3.92 (H5′); $J_{12}$ = 3.4 Hz, $J_{23}$ = 7.7, $J_{34}$ = 6.3, $J_{45}$ < 0.5, $J_{45'}$ = 2.8, $J_{55'}$ = 13.5. Slow-moving in benzene-$d_6$: δ 4.90 (H1), 5.29 (H2), 4.78 (H3), 4.48 (H4), 3.95 (H5), 3.68 (H5′); $J_{12}$ = 3.4 Hz, $J_{23}$ = 7.4, $J_{34}$ = 6.1, $J_{45}$ < 0.5, $J_{45'}$ = 2.9, $J_{55'}$ = 13.6.

The mixed fractions were heated to 50 °C for 5 min with methanol (2 ml) containing 1 drop of 0.1 N hydrochloric acid. This caused a quantitative conversion to *6a* (X = OH), m.p. 147 – 149 °C.

*The ion* 2b *from 3,4-O-benzylidene-2-O-p-toluenesulfonyl-β-D-arabinopyranoside* (1b) was prepared as described above in acetonitrile solution and reacted with a number of nucleophiles. NMR spectra were measured on a solution of *2b* in acetonitrile-$d_3$. $^1$H NMR: δ 4.92 (H1), 4.89 (H2), 6.05 (H3), 5.97 (H4), 4.51 (H5), 4.20 (H5′); $J_{12}$ = 4.0 Hz, $J_{23}$ = 6.5, $J_{34}$ = 7.8, $J_{45} \simeq 0$, $J_{45'}$ = 2.8, $J_{55'}$ = 15.5. $^{13}$C NMR: 95.6 ppm (C1), 74.1 (C2), 84.4 (C3), 87.5 (C4), 55.1 (C5), 182.4 (—C+).

*Reaction with water*. The benzoxonium ion *2b*, prepared from 633 mg of *1b* (X = H) as described above, was stirred for 5 min with aqueous $NaHCO_3$. Work-up as described above and crystallization from ether-pentane gave 454 mg (69 %) of methyl 4-*O*-benzoyl-2-*O*-*p*-toluenesulfonyl-β-D-arabinopyranoside (*6b*, X = OH), m.p. 110 – 113 °C. Two recrystallizations from ethanol gave the pure product, m.p. 114 – 115 °C, $[\alpha]_D^{25}$ −204° (*c* 1.8). Anal. $C_{20}H_{22}O_8S$: C, H, S. $^1$H NMR: δ 4.93 (H1), 4.79 (H2), 4.29 (H3), 5.43 (H4), 3.91 (H5), 3.82 (H5′); $J_{12}$ = 3.5 Hz, $J_{23}$ = 9.8, $J_{34}$ = 3.7, $J_{45}$ = 1.5, $J_{45'}$ = 1.7, $J_{55'}$ = 13.4.

*Bromide ion*. Benzoxonium ion *2b* from 562 mg of *1b* (X = H) was stirred with tetraethylammonium bromide for 4 h. The crude product was crystallized from chloroform to give 376 mg (56 %) of methyl 3-*O*-benzoyl-4-bromo-4-deoxy-2-*O*-*p*-toluenesulfonyl-α-L-xylopyranoside (*4b*, X = Br), m.p. 161 – 163 °C. Three recrystallizations from ethyl acetate-pentane gave a product with m.p. 164 – 165 °C, $[\alpha]_D^{25}$ −62° (*c* 2.4). Anal. $C_{20}H_{21}BrO_7S$: C, H, Br, S. $^1$H NMR: δ 5.04 (H1), 4.51 (H2), 5.73

(H3), 4.0–3.8 (H4,H5,H5′); $J_{12}=3.6$ Hz, $J_{23}=9.7$, $J_{34}\simeq 10$.

Chromatography of the material in the mother liquors gave an additional 32 mg of *4b* (X=Br), 62 mg (11 %) of *6b* (X=OH), and 31 mg (5 %) of methyl 4-*O*-benzoyl-3-bromo-3-deoxy-2-*O*-*p*-toluenesulfonyl-β-D-lyxopyranoside (*5b*, X=Br). This product was only identified through its $^1$H NMR spectrum: δ 4.77 (H1), 5.01 (H2), 4.16 (H3), 5.32 (H4), 4.43 (H5), 3.66 (H5′); $J_{12}=3.4$ Hz, $J_{23}=3.9$, $J_{34}=4.6$, $J_{45}=2.2$, $J_{45'}=3.5$, $J_{55'}=13.0$, $J_{35'}=1.2$.

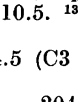
*Thiocyanate ion.* Ion *2b* from 570 mg of *1b* (X=H) was stirred for 5 days with potassium thiocyanate (1.1 g). The crude product was crystallized from chloroform to give 212 mg (33 %) of methyl 3-*O*-benzoyl-4-deoxy-4-thiocyanato-2-*O*-*p*-toluenesulfonyl-α-L-xylopyranoside (*4b*, X=−SCN), m.p. 216–217 °C. Recrystallization from ethyl acetate-pentane gave a product with m.p. 217–218 °C, $[\alpha]_D^{25}$ −46° (*c* 1.4). Anal. $C_{21}H_{21}NO_7S_2$. C, H, N, S. IR: 2155 cm$^{-1}$ (−SCN). $^1$H NMR: δ 4.99 (H1), 4.62 (H2), 5.64 (H3), 3.38 (H4), 3.97 (H5 and H5′); $J_{12}=3.6$ Hz, $J_{23}=9.7$, $J_{34}=10.6$, $J_{45}=8.1$, $J_{45'}=9.2$, $J_{55'}\simeq 12$.

Chromatography of the material in the mother liquor gave three products. The fast-moving fraction (115 mg, 18 %) was methyl 4-*O*-benzoyl-3-deoxy-3-thiocyanato-2-*O*-*p*-toluenesulfonyl-β-D-lyxopyranoside (*5b*, X=−SCN), m.p. 142–143 °C. Recrystallization from ethyl acetate-pentane gave a product with m.p. 143–144 °C, $[\alpha]_D^{25}$ −188° (*c* 1.4). Anal. $C_{21}H_{21}NO_7S_2$: C, H, N, S. IR: 2155 cm$^{-1}$ (−SCN). $^1$H NMR: δ 4.81 (H1), 5.04 (H2), 3.61 (H3), 5.29 (H4), 4.23 (H5), 3.80 (H5′); $J_{12}=3.0$ Hz, $J_{23}=5.0$, $J_{34}=4.3$, $J_{45}=1.5$, $J_{45'}=1.7$, $J_{55'}=13.5$, $J_{35'}=1.7$.

The next fraction was impure *4b* (X=−SCN) (23 mg, 4 %), m.p. 185–210 °C, and the third fraction gave 118 mg (20 %) of the hydrolysis product *4b* (X=OH).

*Trifluoroacetate ion.* The ion *2b* from 485 mg of *1b* (X=H) was stirred overnight with sodium trifluoroacetate (1.0 g). Water (10 drops) was then added and after 2 days at room temperature the mixture deposited 285 mg of crystals, m.p. 200–203 °C. The mother liquor was then worked up as described above. Crystallization from ethyl acetate-pentane gave an additional 95 mg of compound with m.p. 204–206 °C. The combined products were recrystallized from ethyl acetate-pentane to give 286 mg (57 %) of methyl 3-*O*-benzoyl-2-*O*-*p*-toluenesulfonyl-α-L-xylopyranoside (*4b*, X=OH), m.p. 213–214 °C, $[\alpha]_D^{25}$ −136° (*c* 1.3). Anal. $C_{20}H_{22}O_8S$: C, H, S. $^1$H NMR in acetone-$d_6$: δ 4.94 (H1), 4.61 (H2), 5.59 (H3), ~4.0 (H4), 3.76 (H5), 3.63 (H5′); $J_{12}=3.7$ Hz, $J_{23}=10.0$, $J_{34}=8.7$, $J_{45}=5.5$, $J_{45'}=10.8$, $J_{55'}=10.9$.

*Trimethyl phosphite.* Benzoxonium ion *2b* from 570 mg of *1b* (X=H) was treated with 0.5 ml of trimethyl phosphite for 5 min. Tetraethylammonium bromide (1.0 g) was then added and the mixture was stirred overnight. Work-up followed by preparative TLC (ethyl acetate-chloroform 1:1) yielded two diastereomeric methyl 3,4-*O*-(dimethylphosphono-benzylidene)-2-*O*-*p*-toluenesulfonyl-β-D-arabinopyranosides [*1b*, X=−P(O)(OCH$_3$)$_2$]. The fast moving product (197 mg, 27 %) was a syrup, $[\alpha]_D^{20}$ −74° (*c* 1.4). Anal. $C_{22}H_{27}O_{10}PS$: C, H, P. $^1$H NMR: δ 4.62 (H1), 4.06 (H2), 4.63 (H3), 4.94 (H4), 4.12 (H5), 3.93 (H5′); $J_{12}=3.6$ Hz, $J_{23}=7.8$, $J_{34}=5.6$, $J_{45}<0.5$, $J_{45'}=1.8$, $J_{55'}=13.8$, $J_{PH_3}=1.3$, $J_{POCH_3}=10.2$, $^{13}$C NMR: δ 97.0 (C1), 77.8 (C2), 73.6 (C3), 76.7 (C4), 57.7 (C5), 106.8 (  C-P); $J_{CP}=206$ Hz, $J_{P(OCH_3)_2}=7$. $^{31}$P NMR: −14.7 ppm.

The slow moving product (218 mg, 30 %) slowly crystallized. It was recrystallized from ethyl acetate-pentane, m.p. 143–144 °C, $[\alpha]_D^{20}$ −101° (*c* 1.9). Anal. C, H, P. $^1$H NMR: δ 4.82 (H1), 5.11 (H2), 4.47 (H3), 3.93 (H4), 4.11 (H5), 3.84 (H5′); $J_{12}=3.6$ Hz, $J_{23}=7.5$, $J_{34}=6.0$, $J_{45}<0.5$, $J_{45'}=2.8$, $J_{55'}=13.4$, $J_{PH_3}\simeq 0.5$, $J_{POCH_3}=10.5$. $^{13}$C NMR: 97.5 ppm (C1), 78.6 (C2), 74.5 (C3 and C4), 57.4 (C5), 106.7 (  C−P); $J_{CP}=204$ Hz, $J_{P(OCH_3)_2}=7.5$. $^{31}$P NMR: −15.7 ppm.

*Fluoride ion.* Benzoxonium ion *2b* from 531 mg of *1b* (X=H) was stirred for 7 h with sodium fluoride (200 mg). Treatment with trimethyl phosphite and tetraethylammonium bromide and work-up as described above gave 103 mg (15 %) of the fast moving fraction and 177 mg (26 %) of the slow-moving fraction. NMR spectra proved the identity with the products described above.

*Azide ion.* Benzoxonium ion 2b from 514 mg of *1b* (X=H) was stirred for 5 days with sodium azide (1.0 g). Hydrolysis and crystallization gave 351 mg (66 %) of *6b* (X=OH), m.p. 113–114 °C. The product was identical ($^1$H NMR, mixed m.p.) with that described above.

*Phthalimide.* Benzoxonium ion *2b* from 555 mg of *1b* (X=H) was stirred for 24 h with potassium phthalimide (1.0 g). Hydrolysis and crystallization gave 227 mg (39 %) of *6b* (X=OH), m.p. 112–114 °C.

*Acetamide.* To the ion *2b*, from 562 mg of *1b* (X=H), was added acetamide (500 mg) and the solution was kept overnight. Hydrolysis followed by preparative TLC (ether-pentane 4:1) gave four fractions. The fast-moving fraction gave 174 mg (30 %) of *6b* (X=OH), m.p. 113–116 °C. The next fraction, 103 mg, m.p. 190–195 °C, was probably *N*-tritylacetamide as seen from its $^1$H NMR spectrum. The third fraction (73 mg, 11 %) was one of the diastereomeric *N*-acetylated orthoacid amides *1b* (X=CH$_3$CONH−). $^1$H NMR (270 MHz): δ 4.71 (H1), 5.09 (H2), 4.40 (H3), 4.15 (H4), 4.09

(H5), 3.82 (H5′), 1.91 ($H_3CCO$), 7.04 (*NH*); $J_{12}=3.3$ Hz, $J_{23}=6.9$, $J_{34}=5.6$, $J_{45}\simeq 0$, $J_{45'}=2.7$, $J_{55'}=13.5$.

The last fraction (158 mg, 25 %) was the other isomer of *1b* (X = $CH_3CONH-$). $^1H$ NMR (270 MHz): $\delta$ 4.72 (H1), 4.82 (H2), 4.54 (H3), 4.12 (H4), 4.13 (H5), 3.91 (H5′), 1.89 ($H_3CCO$), 6.48 (*NH*); $J_{12}=2.9$ Hz, $J_{23}=6.8$, $J_{34}=6.0$, $J_{45}\simeq 0$, $J_{45'}\simeq 2$, $J_{55'}=13.6$,

When kept in deuteriochloroform solution for 1 – 2 days both products equilibrated to the same 1:1 mixture of diastereomers. Each of the two products was boiled for 5 min with methanol (20 ml) containing 1 drop of 0.1 N HCl. The solutions were then evaporated and the residues were crystallized from ether to give two products with m.p. 108 – 114 and 110 – 114 °C, respectively. The combined products were recrystallized from ethanol-water to give *6b* (X = OH), m.p. 114 – 115 °C, undepressed in admixture with the sample described above.

*Acetate ion.* Benzoxonium ion *2b* from 487 mg of *1b* (X = H) was stirred with anhydrous sodium acetate for 5 days. Work-up and chromatography gave, besides triphenylmethane and triphenylcarbinol, only one fraction (380 mg). $^1H$ NMR spectra showed that this fraction consisted of *6b* (X = OH) mixed with two minor components which were not identified. They contained no acetoxy groups.

In a separate experiment the ion *2b* was prepared in acetonitrile-$d_3$ solution and anhydrous sodium acetate was added. The solution thus obtained probably contained *1b* (X = OAc). $^{13}C$ NMR: 96.3 ppm (C1), 78.6 (C2), 74.6 (C3), 73.8 (C4), 56.6 (C5).

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